(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 750 319 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
31.10.2001 Bulletin 2001/44

(51) Int Cl.[7]: **H01B 7/28**, H01B 3/44

(21) Application number: **96109116.2**

(22) Date of filing: **07.06.1996**

(54) Polymeric composition for coating electric cables having an improved resistance to water treeing and electric cable comprising said composition

Polymere Zusammensetzung zur Beschichtung elektrischer Kabel mit hoher Widerstandsfähigkeit gegenüber der Bildung von Wasserbäumchen und elektrische Kabel mit dieser Zusammensetzung

Composition polymère pour le revêtement de câbles électriques ayant une résistance élevée à la formation d'arborescences et câble électrique comportant cette composition

(84) Designated Contracting States:
DE DK ES FI FR GB IT SE

(30) Priority: **21.06.1995 IT MI951330**

(43) Date of publication of application:
27.12.1996 Bulletin 1996/52

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(56) References cited:
WO-A-93/24940

- **DATABASE WPI Section Ch, Week 8841 Derwent Publications Ltd., London, GB; Class A85, AN 81-74644D XP002014575 & JP-B-63 046 928 (SHOWA ELEC WIRE KK) , 19 September 1988**
- **DATABASE WPI Section Ch, Week 8141 Derwent Publications Ltd., London, GB; Class A85, AN 81-74645D XP002014576 & JP-A-56 107 406 (SHOWA ELEC WIRE KK) , 26 August 1981**

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Printed by Jouve, 75001 PARIS (FR)

Description

[0001] In a general aspect, the present invention relates to electric cables comprising at least one conducting core and at least one insulation coating comprising a polyolefin polymeric base.

[0002] More particularly, the present invention relates to an electric cable comprising an insulation coating having an improved resistance against the formation of the so-called water trees.

[0003] The present invention also relates co a polymeric composition which has a preferred, although not exclusive, use in the manufacture of an insulation coating in electric cables for power transmission at medium or high voltage.

[0004] In the following description, the terms: medium and high voltage, are used to indicate voltages of from 1 to 35 kV and, respectively, over 35 kV.

[0005] As is known, one of the more difficult problems to solve in the manufacture of electric cables for power transmission or energy cable, is that of ensuring that the insulation coating of the conducting core achieves an effective control of the electric field generated during the energy transmission, dissipates as little power as possible and preserves its dielectric and structural characteristics along time.

[0006] It is also known that to obtain such characteristics the best material for manufacturing the insulation coating is constituted by olefin polymers and in particular by polyethylene and copolymers or terpolymers thereof.

[0007] More particularly, among the latter, cross-linked polyethylene - commonly indicated by the acronym XLPE - has either good dieletric characteristics or a low loss factor (minimum dissipated power).

[0008] But together with these good characteristics, olefin polymers generally possess a low resistance against a particular degradation phenomenon, known in the art by the term: "water treeing", which may cause in time a degradation of the electric characteristic of the insulation material.

[0009] Such phenomenon essentially consists in the formation of microfractures having a branched shape (trees), progressively growing in time and responsible, in some cases, for an electric weakening of the insulation coating.

[0010] Even though the mechanism leading to the formation of these microfractures or weak zones has not yet been fully clarified, the formation of such zones or "trees" is anyhow attributed to the combined action of the electric field generated by the current flow in the conducting core of the cable and of the moisture existing in the inside of the insulation coating.

[0011] The problem represented by the formation of the above water trees is particularly felt in the cables for power transmission at medium or high voltage which are not provided with external protection elements, wherein the insulation coating may be directly in touch with water or anyhow with humid environments.

[0012] In order to reduce somehow the formation of water trees, different solutions have been proposed in the art, which are essentially based either on the selection of suitable polymeric materials for the manufacture of the insulation coatings, or on the use of suitable retarding additives, so-called tree-retardants.

[0013] So, for instance, it is known from US Patent 5,246,783 the use of an ethylene copolymer and of an alpha-olefin having 3 to 20 carbon atoms, having a molecular weight distribution of from 1.5 to 30 and a distribution index of the alpha-olefin comonomer greater than 45%.

[0014] European Patent EP 0 179 845 discloses, on the other hand, the combined use of an ethylene polymer or of an ethylene copolymer with an alpha-olefin, with an ethylenealkylacrylate or an ethylene-alkylmethacrylate copolymer, in a cross-linkable coating composition resistant to the formation of water trees, for medium/high voltage energy cables.

[0015] As to the use of the so-called tree-retardant additives, it is known from the US Patents Nos. 4,212,756 and 4,144,202 the use of particular organo silanes comprising an acrylic/methacrylic group and, respectively, an epoxy group.

[0016] Additionally, Japanese patent application JP 56-107405 discloses a composition for power cable insulation which is capable of offering an improved water tree resistance comprising a polyolefin and from 0.5 to 30 parts by weight of an epoxy resin. Among the epoxy resins which may be used diglycidyl ester epoxy is mentioned. According to this reference, the epoxy resin must be uncured if its effectiveness in terms of preventing water trees is to be retained.

[0017] On the other hand, Japanese patent application JP 56-107406 discloses a composition for power cable insulation which is capable of offering an improved water tree resistance comprising from 3 to 50 parts by weight of chlorosulfonated polyethylene and optionally from 0.5 to 30 parts by weight of an uncured epoxy resin per each 100 parts by weight of polyethylene. Among the uncured epoxy resins which may be used diglycidyl ester epoxy is mentioned. Also in this case, the epoxy resin must be uncured if its effectiveness in terms of preventing water trees is to be retained.

[0018] Finally, International PCT application WO 93/24940 discloses a substantially lead-free composition useful as a moisture resistant cable jacket material comprising a curable, extrudable halogenated polymer, an epoxy compound, one or more fillers, one or more plasticizers, means for cross-linking the halogenated polymer, and an accelerator for the cross-linking agent. According to this reference, the epoxy compound performs the function of acid acceptor in the compositions containing halogenated (chlorinated) polymer, thus imparting heat stability to the halogenated polymers during and after processing.

[0019] According to the present invention, it has now been found that the simultaneous presence of ester groups and epoxy groups in a polyolefin polymeric composition introduced by means of a polymeric compound having ester and epoxy groups, may impart to said composition a particular resistance to the phenomenon of water trees in the working condition of an electric cable.

[0020] According to the invention, in fact, a surprising synergistic effect - in terms of increased resistance to the water treeing phenomenon - has been observed, due to the simultaneous presence of ester groups and epoxy groups within a selected concentration range.

[0021] When the aforementioned groups are simultaneously present in the polymeric base forming the insulation coating of the cable, it has been noticed in particular that the retarding effect against water tree formation is evidently greater than the sum of the effects of the same groups when the latter are present alone.

[0022] According to a first aspect thereof, the present invention therefore provides an electric cable comprising at least a conductor and at least an insulation coating consisting essentially of a polymeric composition including a polyolefin polymeric base, said polymeric composition comprising, in parts by weight to the total weight thereof, from 0.5 to 15 parts of ester groups and from 0.01 to 5 parts of epoxy groups, which is characterized in that said amounts of ester and epoxy groups are provided in the polymeric composition by a polymeric compound having ester and epoxy groups, said polymeric compound having a Melt Index of from 0.1 g/10' to 40 g/10'.

[0023] In the following description and the subsequent claims, the term: electric water ageing, is used to indicate an ageing treatment of the insulation coating carried out in water and in the presence of an electric field such as - for instance - the treatment proposed by EFI (Norwegian Electric Power Research Institute), illustrated below, or analogous treatments well known in the art.

[0024] According to a further aspect thereof, the present invention also provides a polyolefin polymeric composition resistant to water treeing, in particular for the manufacture of an insulation coating for electric cables, as defined in attached claim 8.

[0025] In the following description and the subsequent claims, the term: polyolefin polymeric base, is used to indicate a polymer selected from the group comprising high-, medium- and low-density polyethylene homopolymers, ethylene copolymers and ethylene terpolymers with an alpha-olefin having 3 to 20 carbon atoms, ethylene-alpha-olefin-diene terpolymers and mixtures thereof.

[0026] The term: polyolefin polymeric composition, on the other hand, is used to indicate a polymeric composition comprising a polyolefin polymeric base of the above defined type.

[0027] Preferably, the polyolefin polymeric base of the invention is an ethylene polymer selected from the group comprising: polyethylene, copolymers obtainable by polymerizing ethylene with at least one alpha-olefin, linear or branched, having 3 to 14 carbon atoms, terpolymers obtainable by polymerizing ethylene, an alpha-olefin, linear or branched, having 3 to 14 carbon atoms and a diene having 4 to 25 carbon atoms having a density (measured according to ASTM D-792) of from 0.860 g/cm^3 to 0.940 g/cm^3 and a Melt Index (measured according to ASTM D-1238) of from 0.1 g/10' to 40 g/10'.

[0028] In the terpolymers of the invention, the above diene is preferably selected from the group comprising: 1,4 pentadiene, 1,4 hexadiene, 1,5 hexadiene, dicyclopentadiene, 4-vinylcyclohexene, 1-vinyl-1-cyclopentene, ethyl norbornene (LNB), alkylbicyclononadiene, indene, norbornene and mixtures thereof.

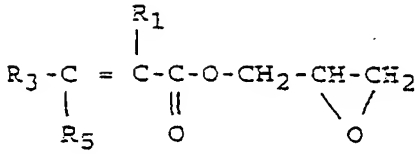
[0029] According to the invention, it has been observed that to achieve an adequate resistance to the water tree formation, the polyolefin matrix forming the insulation coating of the cable conducting core should preferably comprise at least 0.5% by weight of ester groups and at least 0.01% by weight of epoxy groups.

[0030] On the other hand, it has been observed that amounts exceding 15% by weight of ester groups and, respectively, 5% by weight of epoxy groups do not produce a substantial additional benefit in terms of resistance to the phenomenon of water trees; against a marked increase in the power dissipated by the insulation coating (increase of the loss factor or tg delta), with ensuing increase in the energy transmission costs.

[0031] According to the invention, is has also been observed that the aforementioned improved resistance to the water trees formation is not substantially affected by the way in which the ester groups and the epoxy groups are incorporated into the polymeric composition, provided that these groups are present in the aforementioned amounts, as indicated above.

[0032] According to the invention, the aboveidentified minimum amount of ester groups and epoxy groups is reached by adding to a polyolefin polymeric base a polymeric compound, incorporating both an ester group and an epoxy group.

[0033] Bifunctional compounds of preferred and advantageous use are, more particularly, those selected from the group comprising the glycidyl esters of the formula:



(IV)

wherein R_3 and R_5 are independently H, an alkyl or aryl hydrocarbon group, linear or branched, preferably a phenyl, having 1 to 10 carbon atoms; R_1 is H or CH_3.

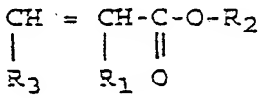
[0034] Among them, the glycidyl esters of the acrylic or methacrylic acid are preferred.

[0035] For the purposes of the invention, particularly preferred is glycidyl methacrylate (GMA), commercially available under the trade name BLEMMER G™ (Blemmer Chemical Corp.).

[0036] Bifunctional compounds of the polymeric type of preferred and advantageous use are those selected from the group comprising:

a) terpolymers obtainable by polymerizing ethylene with:

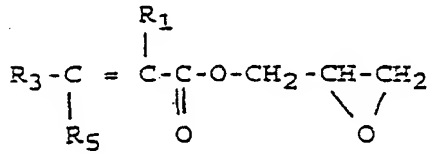
i) at least one acrylic ester of the formula:



(I)

wherein R_1 is H or CH_3, R_2 is an alkyl or aryl hydrocarbon group, linear or branched, preferably a phenyl, having 1 to 10 carbon atoms and R_3 is hydrogen or an alkyl or aryl hydrocarbon group, preferably a phenyl, linear or branched, having 1 to 10 carbon atoms;

ii) at least one glycidyl ester of the formula:

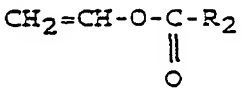


(IV)

wherein the meaning of R_1, R_3 and R_5 are those indicated hereinabove;

b) terpolymers obtainable by polymerizing ethylene with:

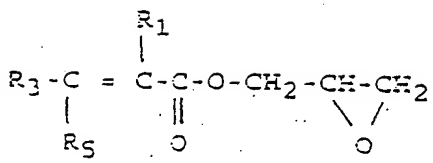
i) at least one vinyl ester of a carboxylic acid of the formula:



(II)

wherein R_2 is an alkyl or aryl hydrocarbon group, linear or branched, preferably a phenyl, having 1 to 10 carbon atoms;

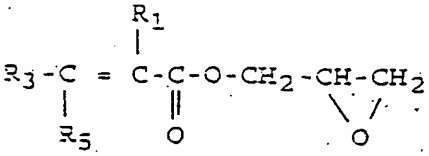
ii) at least one glycidyl ester of the formula:



(IV)

wherein the meaning of R_1, R_3 and R_5 are those indicated hereinabove;

c) copolymers obtainable by polymerizing ethylene with at least one glycidyl ester of the formula:



(IV)

wherein R_3 and R_5 are independently H, an alkyl or aryl hydrocarbon group, linear or branched, preferably a phenyl, having 1 to 10 carbon atoms; R_1 is H or CH_3.

[0037] Glycidyl esters having the formula (IV) of preferred use are the glycidyl esters of the acrylic or methacrylic acids and, particularly, glycidyl methacrylate.

[0038] Ethylene/acrylic ester/glycidyl methacrylate terpolymers and ethylene/glycidyl methacrylate copolymers of preferred and advantageous use are commercially available under the trade names LOTADER™ GMA AX8900 and LOTADER™ GMA AX8840 (Elf Atochem), respectively.

[0039] According to the invention, optimum homogeneity characteristics of the polymeric composition may be obtained when the above bifunctional terpolymers or copolymers have a Melt Index of from 0.1 g/10' to 40 g/10'.

[0040] In this case, the aforementioned amount of ester and epoxy groups may be reached when the polymeric composition comprises from 3 to 30% by weight of at least an ethylene/acrylic ester/glycidyl methacrylate terpolymer or ethylene/vinyl ester/glycidyl methacrylate terpolymer and from 1 to 40% by weight of at least an ethylene/glycidyl methacrylate copolymer.

[0041] Obviously, both the polymeric bifunctional compounds, may be used in the polymeric composition of the invention, so as to reach the desired amount of ester and epoxy groups.

[0042] According to a further aspect thereof, the present invention relates to a new use of one of the above polymeric bifunctional compounds incorporating both an ester group and an epoxy group, as a tree retardant additive in a polymeric composition for coating an electric cable.

[0043] In fact, it is advantageously possible to confer to a polyolefin polymeric base the desired characteristics of resistance to the water treeing phenomenon by simply adding said bifunctional compounds to said base in the aforementioned amounts.

[0044] Preferably, the amount of the ester and epoxy groups falls within said range of 0.5-15% parts by weight and, respectively, of 0.01-5% parts by weight to the total weight of the composition so obtained.

[0045] In a preferred embodiment, the polymeric composition of the invention is cross-linked by means of one of the methods known in the art to this end.

[0046] Preferably, the polymeric composition is chemically cross-linked; for this purpose, it incorporates an effective amount of at least one cross-linking agent, such as for instance tert-butyl-cumyl peroxide.

[0047] In order to achieve an improved stability, furthermore, the polymeric composition of the invention advantageously incorporates an effective amount of at least one antioxidant agent, such as for instance 4,4'-thio-bis(3-methyl-6-ter-butyl)phenol.

[0048] Depending upon the particular use of the cable, moreover, the polymeric composition of the invention may incorporate other additives and fillers conventional in themselves, such as for instance pigments, dyes, stabilizers, lubricants.

[0049] Further advantages and characteristics of the invention will be better apparent from the following description of some preferred embodiments thereof, which are reported in the following by way of non-limitative illustration, with reference to the attached drawing, whose only figure shows, in perspective view and partial cross-section, a cable according to the invention.

[0050] In such figure, reference 1 indicates a cable comprising an electric conducting core 2 including a plurality of wires, i.e. of copper, all indicated by 3.

[0051] The conducting core 2 is enclosed within several coaxial coating layers, including an inner semiconducting layer 4, an insulation layer 5, an outer semiconducting layer 6, a metal screen 7 and an outer polymeric sheath 8.

[0052] The above described cable 1 may be produced starting from the conducting core 2 according to known methods, for instance by subsequently extruding layers 4, 5 and 6, by applying the metal screen 7 and by finally extruding the external sheath 8.

[0053] With reference to the description hereinabove, some merely illustrative and not limitative examples of polymeric compositions according to the invention, particularly suitable for the manufacture of the insulation layer of a cable, such as for instance the layer 5 of the cable described above, will be provided in the following.

EXAMPLE 1

[0054] A polymeric composition according to the invention was prepared by mixing in an extruder the following ingredients, in parts by weight for each 100 pares of polymeric base (phr) :

polymeric base	90 phr
ethylene/acrylic ester/glycidyl methacrylate terpolymer	10 phr
peroxide	2 phr
antioxidant	0.34 phr

[0055] As polymeric base low-density polyethylene (LDPE) was used, having a density of 0.923 g/cm^3 and a Melt Flow Index of 2 g/10' (Enichem).

[0056] As ethylene/acrylic ester/glydidyl methacrylate terpolymer, LOTADER™ GMA AX8900™ (Elf Atochem) was used.

[0057] The peroxide and the antioxidant used were tert-butyl-cumyl peroxide (TRIGONOX™ T produced by AKZO) and 4-4'-chio-bis(3-methyl-6-ter-butyl)phenol (SANTONOX™R produced by MONSANTO).

EXAMPLE 2

[0058] According to the same preparation methods and using the same ingredients as the previous Example 1, a polymeric composition was prepared having the following composition in parts by weight for each 100 parts of polymeric base (phr):

polymeric base	85 phr
ethylene/acrylic ester/glycidyl methacrylate terpolymer	15 phr
peroxide	2 phr
antioxidant	0.34 phr

EXAMPLE 3

[0059] According to the same preparation methods and using the same ingredients as the previous Example 1, a polymeric composition was prepared having the following composition in parts by weight for each 100 parts of polymeric base (phr):

polymeric base	80 phr
ethylene/acrylic ester/glycidyl methacrylate terpolymer	20 phr
peroxide	2 phr
antioxidant	0.34 phr

EXAMPLE 4

(Comparison)

[0060] According to conventional preparation methods known in the art and using the same ingredients of the previous Example 1, a polymeric composition including only the polyolefin polymer, the cross-linking agent and the anti-

oxidant agent was prepared, having the following composition in parts by weight for each 100 parts of polymeric base (phr) :

polymeric base	100 phr
peroxide	2 phr
antioxidant	0.34 phr

EXAMPLE 5

(Comparison)

[0061] According to conventional preparation methods known in the art and using the same ingredients of the previous Example 1, a polymeric composition including acrylic ester groups was prepared, having the following composition in parts by weight for each 100 parts of polymeric base (phr):

polymeric base	82.5 phr
ethylene/acrylic-ester copolymer	17.5 phr
peroxide	2 phr
antioxidant	0.34 phr

[0062] As ethylene/acrylic-ester copolymer the ethylene/butyl acrylate copolymer commercially available under the trade name ENATHENE™ EA 720 (USI QUANTUM) was used.

EXAMPLE 6

(Comparison)

[0063] According to conventional preparation methods known in the art and using the same ingredients of the previous Example 1, a polymeric composition according to the prior art and including epoxy groups was prepared, having the following composition in parts by weight for each 100 parts of polymeric base (phr):

polymeric base	100 phr
epoxy resin	1.5 phr
peroxide	2 phr
antioxidant	0.34 phr

[0064] As epoxy resin the resin commercially available under the trade name EUREPOX™ (SCHERING) was used.

EXAMPLE 7

(Evaluation of the water tree resistance)

[0065] The resistance properties to the formation of water trees of the polymeric compositions according to Examples 1-6 hereinabove, were evaluated according to the methodology proposed by EFI (Norwegian Electric Power Research Institute) in the publication "The EFI Test Method for Accelerated Growth of Water Trees", presented at the "1990 IEEE International Symposium on Electrical Insulation", held in Toronto, Canada, on 3-6 June 1990.

[0066] According to such a methodology, the cable is simulated by preparing cup-shaped multilayered test-samples, wherein the material constituting the insulation coating is sandwiched between two layers of semiconducting material.

[0067] More particularly, the layer of insulation material is heat-moulded in the shape of a cup at the temperature of 120°C, starting from a tape having a thickness of 5-7 mm, in an electric press capable of developing a pressure of about 90 t, so as to obtain a thickness of about 0.50 mm.

[0068] The layers of semiconducting material, extruded and preshaped in an analogous way until a thickness of about 0.5 mm is obtained, are then pressed and heat-welded on opposite sides of the insulation layer at a temperature of about 180°C for 15 minutes in an electric press similar to that used to form the same layers.

[0069] The test-samples so obtained, once cooled at room temperature, are then submitted to an accelerated electric ageing test, filling with water the cavity defined inside the cup-shaped test-sample, immersing in the water a high

voltage electrode and [illegible]ng the resulting equipment on a metal plate- (earth electrode).

[0070] The accelerated trees growth is then induced in the insulation layer by applying a voltage generally of from 2 to 15 kV between the electrodes.

[0071] In order to further accelerate the phenomenon, the test is heat-performed, for instance in a suitable oven.

[0072] In the tests carried out, the polymeric compositions of Examples 1-6 were coupled to a semiconducting screen constituted by a XLPE mix, commercially available under the trade name NCPE 0592™ (Borealis N.V., Bruxelles, Belgium).

[0073] According to the above described EFI methodology, 5 test-samples were produced for each polymeric composition, which were submitted to accelerated ageing in the following test conditions:

- electric gradient: 5 kV/mm
- temperature: 70°C

[0074] At the end of a 30-day period, 20 100 µm-thick sections were taken off from each test-piece, dyed with methylene blue according co the CIGRE standards and then examined with an optical microscope at a magnification of from 100 to 200X.

[0075] From such observation the density of water trees, expressed in number of trees per cm^3, was then calculated for each test-sample. The mean values are shown in the following Table 1.

TABLE 1

Example nr.	1	2	3	4	5	6
Trees density (nr./cm^3)	190	140	95	980	470	780

[0076] From the data shown in the table, it may be observed that the resistance to the water tree formation of the polymeric compositions of the invention (Examples 1-3), comprising ester groups and epoxy groups, is markedly greater that that offered by the control polymeric compositions, incorporating only acrylic groups (Example 5) or epoxy groups (Example 6).

[0077] In this connection, it has to be observed that, quite surprisingly, the combined effects of the above ester groups and epoxy groups is of a synergistic type, i.e., much greater than the sum of the individual effects ascribable to each of them considered in isolation.

[0078] This synergistic effect is so marked that, in the case of the composition of Example 3, a density of water trees has been observed whose order of magnitude was even lower than that of the cross-linked polyethylene taken as control.

EXAMPLE 8

(Evaluation of dielectric strength)

[0079] The dielectric strength properties of the polymeric compositions according to the previous Examples 1-6 were evaluated on test-samples obtained by the ageing methodology proposed by EFI, described in the preceding example.

[0080] In this case, 20 test-samples were produced which were submitted to accelerated water ageing in the following test conditions:

- electric gradient: 5 kV/mm
- temperature: 70°C

[0081] On a batch of 5 non-aged test-samples (control) and on three batches of 5 test-samples taken after 7, 15 and 30 days respectively from the beginning of the accelerated electric ageing, the value of the dielectric strength was then measured according to the ASTM D-149 standard.

[0082] The dielectric strength tests were carried out with silicone oil in the inside and on the outside of the test-samples, using a circular electrode and applying a voltage gradient of 2 kV/s.

[0083] The results of the tests carried out (mean values of 5 tests) are shown in the following Table 2.

TABLE 2

Example		1	2	3	4	5	6
	as is	120	130	135	105	120	110

TABLE 2 (continued)

Example		1	2	3	4	5	6
Strength	7 days	60	75	85	55	60	58
(kV/mm)	15 days	55	70	80	45	50	47
	30 days	55	70	75	45	50	47

From the data shown in the table, it may be observed that - after ageing - the dielectric strength of the polymeric compositions of the invention (Examples 1-3), is as a whole greater than that of the control compositions, independently from the original starting values, with an advantageous improvement of the insulating properties of the composition.

EXAMPLE 9

(Evaluation of the loss factor)

[0084] The evaluation of the so-called loss factor (tan delta) of the polymeric compositions according to the previous Examples 1-6 was carried out according to the ASTM D-150 standard (AC Loss Characteristics and Dielectric Constant (Permettivity) of Solid Electrical Insulating Material).

[0085] More particularly, the loss factor was measured by using as test-samples moulded flat plates of 20 x 20 cm of side, 1.0 mm thick, and using circular electrodes with guard ring.

[0086] Before taking the measures, the test-samples had been submitted to heat treatment at 90°C in order to remove the cross-linking by-products in each plate.

[0087] The results of the tests performed (mean values out of 5 tests) are shown in the following Table 3.

TABLE 3

Example nr.	1	2	3	4	5	6
tg delta (room T)	0.0002	0.0003	0.0004	0.0001	0.0001	0.0010
tg delta (90°C)	0.0008	0.0024	0.0110	0.0003	0.0004	0.0110

[0088] As it may be observed from the above table, the presence of ester groups and epoxy groups in the polymeric composition of the invention may bring about an increase in the loss factor; hence, the content of said groups may be selected having regard to the desired resistance characteristics to the formation of water trees and to the other performances required to the cable.

[0089] To this end, the optimum amount of ester groups and epoxy groups in the polymeric composition may be selected by a man skilled in the art in relation to the specific application requirements of the cable.

[0090] From what has been described and illustrated above it is immediately evident that the cable of the invention possesses a combination of features that render the same useable for all those applications - and in particular for power transmission at medium/high voltage - where a particular resistance to water treeing is required.

[0091] In particular, according to the invention, the use of ester groups and epoxy groups in predetermined amount in a given polymeric composition allows to increase the resistance to the phenomenon of water treeing compared to the case when - in the same polymeric composition - such groups are not present and, as a consequence, to increase, after electric water ageing, the dielectric strength of the insulation coating of a cable manufactured with the same polymeric base.

[0092] Obviously, those skilled in the art may introduce variants and modifications to the above described invention, in order to satisfy specific and contingent requirements, variants and modifications which fall anyhow within the scope of protection as is defined in the following claims.

Claims

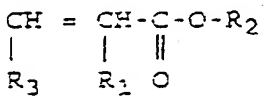
1. An electric cable comprising at least one conducting core (2) and at least one insulation coating (5) consisting essentially of a polymeric composition including a polyolefin polymeric base, said polymeric composition comprising, in parts by weight to the total weight thereof, from 0.5 to 15 parts of ester groups and from 0.01 to 5 parts of epoxy groups,
characterized in that said amounts of ester and epoxy groups are provided in the polymeric composition by a

polymeric compound having ester and epoxy groups, said polymeric compound having a Melt Index of from 0.1 g/10' to 40 g/10'.

2. An electric cable according to claim 1, **characterized in that** said polymeric compound is selected from the group comprising:

a) a terpolymer obtainable by polymerizing ethylene with

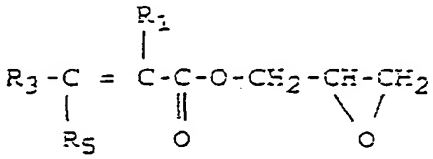
i) at least one acrylic ester of the formula:



(I)

wherein R_1 is H or CH_3, R_2 is an alkyl or aryl hydrocarbon group, linear or branched, preferably a phenyl, having 1 to 10 carbon atoms, and R_3 is hydrogen or an alkyl or aryl hydrocarbon group, linear or branched, preferably a phenyl, having 1 to 10 carbon atoms; and

ii) at least one glycidyl ester of the formula:

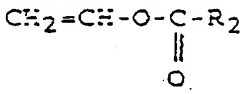


(IV)

wherein R_3 and R_5 are independently H, an alkyl or aryl hydrocarbon group, linear or branched, preferably a phenyl, having 1 to 10 carbon atoms; R_1 is H or CH_3;

b) a terpolymer obtainable by polymerizing ethylene with

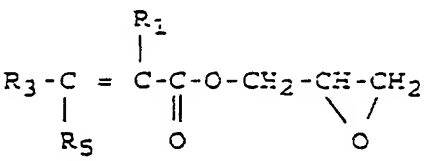
i) at least one vinyl ester of a carboxylic acid of the formula:



(II).

wherein R_2 is an alkyl or aryl hydrocarbon group, linear or branched, preferably a phenyl, having 1 to 10 carbon atoms; and

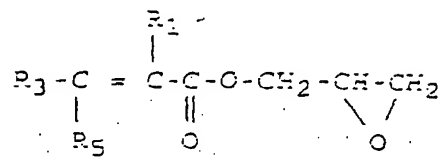
ii) at least one glycidyl ester of the formula:



(IV)

wherein R_3 and R_5 are independently H, an alkyl or aryl hydrocarbon group, linear or branched, preferably a phenyl, having 1 to 10 carbon atoms; R_1 is H or CH_3;

c) a copolymer obtainable by polymerizing ethylene with at least one glycidyl ester of the formula



(IV)

wherein R_3 and R_5 are independently H, an alkyl or aryl hydrocarbon group, linear or branched, preferably a phenyl, having 1 to 10 carbon atoms; R_1 is H or CH_3.

3. An electric cable according to claim 1, **characterized in that** said polyolefin polymeric base comprises a polymer selected from the group comprising high-, medium- and low-density polyethylene homopolymers, ethylene copolymers and ethylene terpolymers with an alpha-olefin having 3 to 20 carbon atoms, ethylene-alpha-olefin-diene terpolymers and mixtures thereof.

4. An electric cable according to claim 2, **characterized in that** said at least one glycidyl ester is glycidyl methacrylate.

5. An electric cable according to anyone of the preceding claims, **characterized in that** said polyolefin polymeric base further comprises an effective amount of at least one cross-linking agent.

6. An electric cable according to claim 5, **characterized in that** said at least one cross-linking agent is tert-butyl-cumyl peroxide.

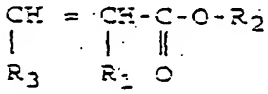
7. An electric cable according to anyone of the preceding claims, **characterized in that** said polyolefin polymeric base further comprises an effective amount of at least one antioxidant agent.

8. A polyolefin polymeric composition resistant to water treeing, in particular for the manufacture of an insulating coating for electric cables, including a polyolefin polymeric base, said polymeric composition comprising, in parts by weight to the total weight thereof, from 0.5 to 15 parts of ester groups and from 0.01 to 5 parts of epoxy groups, **characterized in that** said amounts of ester and epoxy groups are provided in the polymeric composition by a polymeric compound having ester and epoxy groups, said polymeric compound having a Melt Index of from 0.1 g/10' to 40 g/10'.

9. A polymeric composition according to claim 8, **characterized in that** said polymeric compound is selected from the group comprising:

a) a terpolymer obtainable by polymerizing ethylene with

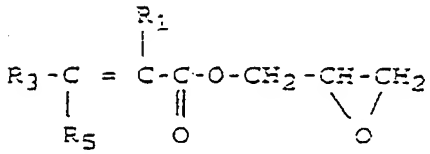
i) at least one acrylic ester of the formula:



(I)

wherein R_1 is H or CH_3, R_2 is an alkyl or aryl hydrocarbon group, linear or branched, preferably a phenyl, having 1 to 10 carbon atoms, and R_3 is hydrogen or an alkyl or aryl hydrocarbon group, linear or branched, preferably a phenyl, having 1 to 10 carbon atoms; and

ii) at least one glycidyl ester of the formula:

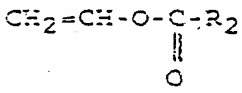


(IV)

wherein R_3 and R_5 are independently H, an alkyl or aryl hydrocarbon group, linear or branched, preferably a phenyl, having 1 to 10 carbon atoms; R_1 is H or CH_3;

b) a terpolymer obtainable by polymerizing ethylene with

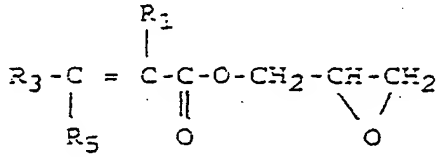
i) at least one vinyl ester of a carboxylic acid of the formula:



(II)

wherein R_2 is an alkyl or aryl hydrocarbon group, linear or branched, preferably a phenyl, having 1 to 10 carbon atoms; and

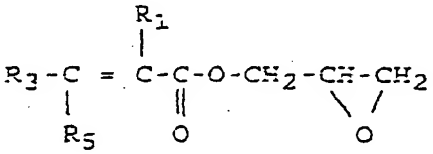
ii) at least one glycidyl ester of the formula:



(IV)

wherein R_3 and R_5 are independently H, an alkyl or aryl hydrocarbon group, linear or branched, preferably a phenyl, having 1 to 10 carbon atoms; R_1 is H or CH_3;

c) a copolymer obtainable by polymerizing ethylene with at least one glycidyl ester of the formula



(IV)

wherein R_3 and R_5 are independently H, an alkyl or aryl hydrocarbon group, linear or branched, preferably a phenyl, having 1 to 10 carbon atoms; R_1 is H or CH_3.

10. A polymeric composition according to claim 8, **characterized in that** it comprises a polymer selected from the group comprising high-, medium- and low-density polyethylene homopolymers, ethylene copolymers and ethylene terpolymers with an alpha-olefin having 3 to 20 carbon atoms, ethylene-alpha-olefin-diene terpolymers and mixtures thereof.

11. A polymeric composition according to claim 9, **characterized in that** said at least one glycidyl ester is glycidyl methacrylate.

12. A polymeric composition according to anyone of the preceding claims 8-11, **characterized in that** it further comprises an effective amount of at least one cross-linking agent.

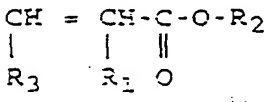
13. A polymeric composition according to claim 12, **characterized in that** said at least cross-linking agent is tert-butyl-cumyl peroxide.

14. A polymeric composition according to anyone of the preceding claims 8-13, **characterized in that** it further comprises an effective amount of at least one antioxidant agent.

15. Use of a polymeric composition according to anyone of claims 8-14 for the insulation of electric cables.

16. Use of a terpolymer obtainable by polymerizing ethylene with

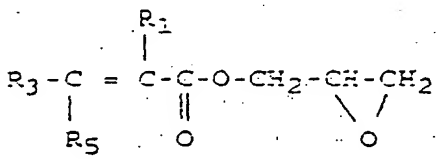
i) at least one acrylic ester of the formula:



(I)

wherein R_1 is H or CH_3, R_2 is an alkyl or aryl hydrocarbon group, linear or branched, preferably a phenyl, having 1 to 10 carbon atoms, and R_3 is hydrogen or an alkyl or aryl hydrocarbon group, linear or branched, preferably a phenyl, having 1 to 10 carbon atoms; and

ii) at least one glycidyl ester of the formula:



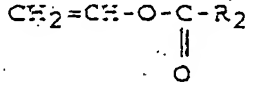
(IV)

wherein R_3 and R_5 are independently H, an alkyl or aryl hydrocarbon group, linear or branched, preferably a phenyl, having 1 to 10 carbon atoms; R_1 is H or CH_3,

as tree retardant additive in a polymeric composition for coating an electric cable.

17. Use of a terpolymer obtainable by polymerizing ethylene with

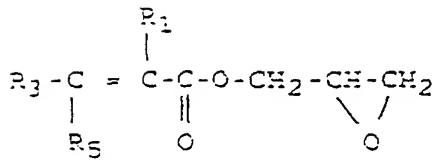
i) at least one vinyl ester of a carboxylic acid of the formula:



(II)

wherein R_2 is an alkyl or aryl hydrocarbon group, linear or branched, preferably a phenyl, having 1 to 10 carbon atoms; and

ii) at least one glycidyl ester of the formula:



(IV)

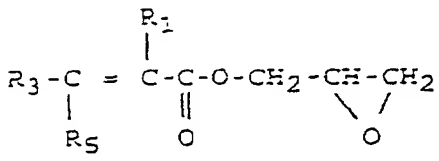
wherein R_3 and R_5 are independently H, an alkyl or aryl hydrocarbon group, linear or branched, preferably a phenyl, having 1 to 10 carbon atoms; R_1 is H or CH_3,

as tree retardant additive in a polymeric composition for coating an electric cable.

18. Use according to claims 16 or 17, **characterized in that** said terpolymer has a Melt Index of from 0.1 g/10' to 40 g/10'.

19. Use according to claims 16 or 17, **characterized in that** said at least one glycidyl ester is glycidyl methacrylate.

20. Use of a copolymer obtainable by polymerizing ethylene with at least one glycidyl ester of the formula:



(IV)

wherein R_3 and R_5 are independently H, an alkyl or aryl hydrocarbon group, linear or branched, preferably a phenyl, having 1 to 10 carbon atoms; R_1 is H or CH_3,
as tree retardant additive in a polymeric composition for coating an electric cable.

21. Use according to claim 20, **characterized in that** said at least one glycidyl ester is glycidyl methacrylate.

22. Use according to claim 20, **characterized in that** said copolymer has a Melt Index of from 0.1 g/10' to 40 g/10'.

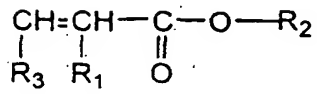
Patentansprüche

1. Elektrisches Kabel, umfassend zumindest einen leitenden Kern (2) und zumindest eine Isolierbeschichtung (5), im wesentlichen bestehend aus einer polymeren Zusammensetzung, umfassend eine polymere Polyolefinbasis, wobei die polymere Zusammensetzung von 0,5 bis 15 Teilen Estergruppen und von 0,01 bis 5 Teilen Epoxygruppen umfasst, als Gewichtsteile bezogen auf das Gesamtgewicht davon,
dadurch gekennzeichnet, dass
die Mengen der Ester- und Epoxygruppen in der polymeren Zusammensetzung durch eine polymere Verbindung mit Ester- und Epoxygruppen zur Verfügung gestellt werden, wobei die polymere Verbindung einen Schmelzindex von 0,1 g/10 min bis 40 g/10 min aufweist.

2. Elektrisches Kabel nach Anspruch 1,
dadurch gekennzeichnet, dass
die polymere Verbindung aus der Gruppe ausgewählt ist, umfassend

a) ein Terpolymer, erhältlich durch Polymerisation von Ethylen mit

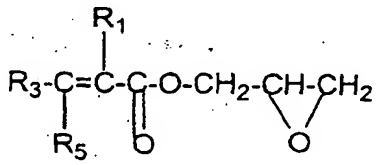
i) zumindest einem Acrylester der Formel:



(I)

worin R_1H oder CH_3, R_2 eine Alkyl- oder Aryl-Kohlenwasserstoffgruppe, linear oder verzweigt, bevorzugt Phenyl, mit 1 bis 10 Kohlenstoffatomen und R_3 Wasserstoff oder eine Alkyl- oder Aryl-Kohlenwasserstoffgruppe, linear oder verzweigt, bevorzugt eine Phenylgruppe, mit 1 bis 10 Kohlenstoffatomen ist; und

ii) zumindest einem Glycidylester der Formel:

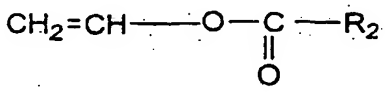


(IV)

worin R_3 und R_5 unabhängig H, eine Alkyl- oder Aryl-Kohlenwasserstoffgruppe, linear oder verzweigt, bevorzugt ein Phenyl, mit 1 bis 10 Kohlenstoffatomen, R_1 H oder CH_3 sind;

b) ein Terpolymer, erhältlich durch Polymerisation von Ethylen mit

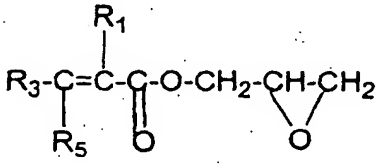
i) zumindest einem Vinylester einer Carbonsäure mit der Formel:



(II)

worin R_2 eine Alkyl- oder Aryl-Kohlenwasserstoffgruppe, linear oder verzweigt, bevorzugt ein Phenyl, mit 1 bis 10 Kohlenstoffatomen ist; und

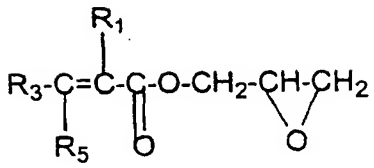
ii) zumindest einem Glycidylester der Formel:



(IV)

worin R_3 und R_5 unabhängig H, eine Alkyl- oder Aryl-Kohlenwasserstoffgruppe, linar oder verzweigt, bevorzugt ein Phenyl, mit 1 bis 10 Kohlenstoffatomen, R_1 H oder CH_3 sind;

c) einen Copolymer, erhältlich durch Polymerisation von Ethylen mit zumindest einem Glycidylester der Formel:



(IV)

worin R_3 und R_5 unabhängig H, ein Alkyl- oder Aryl-Kohlenwasserstoffgruppe, linear oder verzweigt, bevorzugt ein Phenyl, mit 1 bis 10 Kohlenstoffatomen; R_1 H oder CH_3 sind.

3. Elektrisches Kabel nach Anspruch 1,
dadurch gekennzeichnet, dass
die polymere Polyolefinbasis ein Polymer umfasst, ausgewählt aus der Gruppe, umfassend Homopolymere aus Polyethylen hoher, mittlerer und niedriger Dichte, Ethylencopolymere und Ethylenterpolymere mit einem alpha-Olefin mit 3 bis 20 Kohlenstoffatomen, Ethylen-alpha-Olefin-Dien-Terpolymere und Mischungen davon.

4. Elektrisches Kabel nach Anspruch 2,
dadurch gekennzeichnet, dass
der zumindest eine Glycidylester Glycidylmethacrylat ist.

5. Elektrisches Kabel nach einem der vorhergehenden Ansprüche,
dadurch gekennzeichnet, dass
die polymere Polyolefinbasis weiterhin eine effektive Menge von zumindest einem Vernetzungsmittel umfasst.

6. Elektrisches Kabel nach Anspruch 5,
dadurch gekennzeichnet, dass
das zumindest eine Vernetzungsmittel tert-Butylcumylperoxid ist.

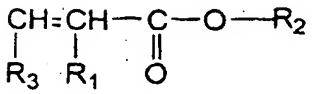
7. Elektrisches Kabel nach einem der vorhergehenden Ansprüche,
dadurch gekennzeichnet, dass
die polymere Polyolefinbasis weiterhin eine effektive Menge von zumindest einem Antioxidans enthält.

8. Polymere Polyolefinzusammensetzung, die gegenüber Wasserbäumchen resistent ist, insbesondere zur Herstellung einer Isolierbeschichtung für elektrische Kabel, umfassend eine polymere Polyolefinbasis, wobei die polymere Zusammensetzung von 0,5 bis 15 Teile Estergruppen und von 0,01 bis 5 Teile Epoxygruppen, als Gewichtsteile, bezogen auf das Gesamtgewicht davon enthält,
dadurch gekennzeichnet, dass
die Mengen der Ester- und Epoxygruppen in der polymeren Zusammensetzung durch eine polymere Verbindung mit Ester- und Epoxygruppen zur Verfügung gestellt werden, wobei die polymere Verbindung einen Schmelzindex von 0,1 g/10 min bis 40 g/10 min hat.

9. Polymere Zusammensetzung nach Anspruch 8,
dadurch gekennzeichnet, dass
die polymere Verbindung ausgewählt ist aus der Gruppe, umfassend:

a) ein Terpolymer, erhältlich durch Polymerisation von Ethylen mit

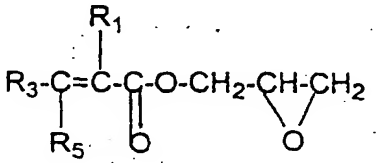
i) zumindest einem Acrylester der Formel:



(I)

worin R_1 H oder CH_3, R_2 eine Alkyl- oder Aryl-Kohlenwasserstoffgruppe, linear oder verzweigt, bevorzugt ein Phenyl, mit 1 bis 10 Kohlenstoffatomen und R_3 Wasserstoff oder eine Alkyl- oder Aryl-Kohlenwasserstoffgruppe, linear oder verzweigt, bevorzugt ein Phenyl mit 1 bis 10 Kohlenstoffatomen ist; und

ii) zumindest einem Glycidylester der Formel:

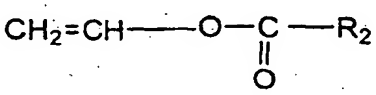


(IV)

worin R_3 und R_5 unabhängig H, eine Alkyl- oder Aryl-Kohlenwasserstoffgruppe, linear oder verzweigt, bevorzugt ein Phenyl, mit 1 bis 10 Kohlenstoffatomen, R_1 H oder CH_3 sind;

b) ein Terpolymer, erhältlich durch Polymerisation von Ethylen mit

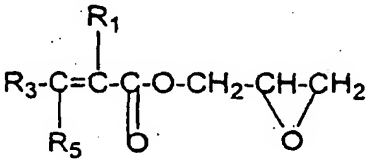
i) zumindest einem Vinylester einer Carbonsäure mit der Formel:



(II)

worin R_2 eine Alkyl- oder Aryl-Kohlenwasserstoffgruppe, linear oder verzweigt, bevorzugt ein Phenyl, mit 1 bis 10 Kohlenstoffatomen ist; und

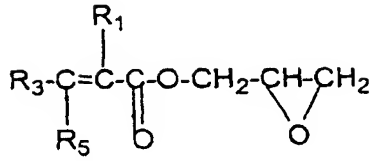
ii) zumindest einem Glycidylester der Formel:



(IV)

worin R_3 und R_5 unabhängig H, eine Alkyl- oder Aryl-Kohlenwasserstoffgruppe, linar oder verzweigt, bevorzugt ein Phenyl, mit 1 bis 10 Kohlenstoffatomen, R_1 H oder CH_3 sind;

c) ein Copolymer, erhältlich durch Polymerisation von Ethylen mit zumindest einem Glycidylester der Formel:



(IV)

worin R_3 und R_5 unabhängig H, eine Alkyl- oder Aryl-Kohlenwasserstoffgruppe, linear oder verzweigt, bevorzugt ein Phenyl, mit 1 bis 10 Kohlenstoffatomen; R_1 H oder CH_3 sind.

10. Polymere Zusammensetzung nach Anspruch 8,
dadurch gekennzeichnet, dass
sie ein Polymer umfasst, ausgewählt aus der Gruppe, umfassend Homopolymere aus Polyethylen hoher, mittlerer und niedriger Dichte, Ethylencopolymere und Ethylenterpolymere mit einem alpha-Olefin mit 3 bis 20 Kohlenstoffatomen, Ethylen-alpha-Olefin-Dien-Terpolymere und Mischungen davon.

11. Polymere Zuammensetzung nach Anspruch 9,
dadurch gekennzeichnet, dass
der zumindest eine Glycidylester Glycidylmethacrylat ist.

12. Polymere Zusammensetzung nach einem der vorhergehenden Ansprüche8 bis 11,
dadurch gekennzeichnet, dass
sie weiterhin eine effektive Menge von zumindest einem Vernetzungsmittel umfasst.

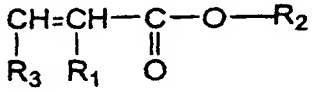
13. Polymere Zusammensetzung nach Anspruch 12,
dadurch gekennzeichnet, dass
das zumindest eine Vernetzungsmittel tert-Butylcumylperoxid ist.

14. Polymere Zusammensetzung nach einem der vorhergehenden Ansprüche 8 bis 13,
dadurch gekennzeichnet, dass
sie weiterhin eine effektive Menge von zumindest einem Antioxidans enthält.

15. Verwendung einer polymeren Zusammensetzung nach einem der Ansprüche 8 bis 14 zur Isolierung von elektrischen Kabeln.

16. Verwendung eines Terpolymers, erhältlich durch Polymerisation von Ethylen mit

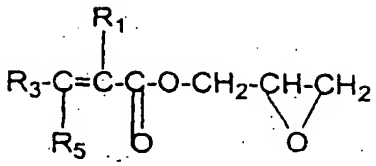
i) zumindest einem Acrylester der Formel:



(I)

worin R_1 H oder CH_3, R_2 eine Alkyl- oder Aryl-Kohlenwasserstoffgruppe, linear oder verzweigt, bevorzugt ein Phenyl, mit 1 bis 10 Kohlenstoffatomen und R_3 Wasserstoff oder eine Alkyl- oder Aryl-Kohlenwasserstoffgruppe, linear oder verzweigt, bevorzugt ein Phenyl, mit 1 bis 10 Kohlenstoffatomen ist; und

ii) zumindest einem Glycidylester der Formel:



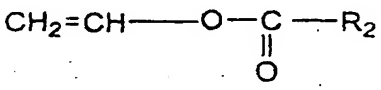
(IV)

worin R_3 und R_5 unabhängig H, eine Alkyl- oder Aryl-Kohlenwasserstoffgruppe, linear oder verzweigt, bevorzugt ein Phenyl, mit 1 bis 10 Kohlenstoffatomen, R_1 H oder CH_3 sind

als Baumverzögerungsadditiv in einer polymeren Zusammensetzung zur Beschichtung eines elektrischen Kabels.

17. Verwendung eines Terpolymers, erhältlich durch Polymerisation von Ethylen mit

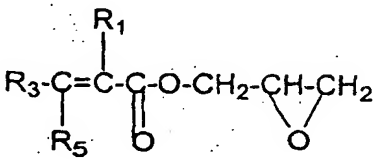
i) zumindest einem Vinylester einer Carbonsäure mit der Formel:



(II)

worin R_2 eine Alkyl- oder Aryl-Kohlenwasserstoffgruppe, linear oder verzweigt, bevorzugt ein Phenyl, mit 1 bis 10 Kohlenstoffatomen ist; und

ii) zumindest einem Glycidylester der Formel:



(IV)

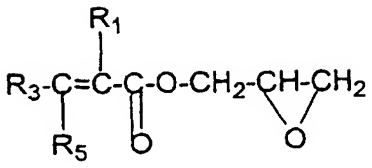
worin R_3 und R_5 unabhängig H, eine Alkyl- oder Aryl-Kohlenwasserstoffgruppe, linar oder verzweigt, bevorzugt ein Phenyl, mit 1 bis 10 Kohlenstoffatomen, R_1 H oder CH_3 sind;

als Baumverzögerungsadditiv in einer polymeren Zusammensetzung zur Beschichtung eines elektrischen Kabels.

18. Verwendung nach den Ansprüchen 16 oder 17,
dadurch gekennzeichnet, dass
das Terpolymer einen Schmelzindex von 0,1 g/10 min bis 40 g/10 min hat.

19. Verwendung nach den Ansprüchen 16 oder 17,
dadurch gekennzeichnet, dass
der zumindest eine Glycidylester Glycidylmethacrylat ist.

20. Verwendung eines Copolymers, erhältlich durch Polymerisation von Ethylen mit zumindest einem Glycidylester der Formel:



(IV)

worin R_3 und R_5 unabhängig H, eine Alkyl- oder Aryl-Kohlenwasserstoffgruppe, linar oder verzweigt, bevorzugt ein Phenyl, mit 1 bis 10 Kohlenstoffatomen, R_1 H oder CH_3 sind;
als Baumverzögerungsadditiv in einer polymeren Zusammensetzung zur Beschichtung eines elektrischen Kabels.

21. Verwendung nach Anspruch 20,
dadurch gekennzeichnet, dass
der zumindest eine Glycidylester Glycidylmethacrylat ist.

22. Verwendung nach Anspruch 20,
dadurch gekennzeichnet, dass
das Copolymer einen Schmelzindex von 0,1 g /10 min bis 40 g/10 min hat.

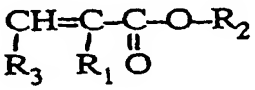
Revendications

1. Câble électrique comportant au moins une âme conductrice (2) et au moins une gaine isolante (5) essentiellement constituée d'une composition de polymère contenant . e base polymère en polyoléfine, cette composition de polymère comportant, en parties en poids rapportées à son poids total, de 0,5 à 15 parties de groupes esters et de 0,01 à 5 parties de groupes époxy,
caractérisé en ce que ces quantités de groupes ester et de groupes époxy sont apportées dans la composition de polymère par un composé polymère qui comporte des groupes ester et des groupes époxy et dont l'indice de fluidité à chaud vaut de 0,1 à 40 g/10 min.

2. Câble électrique conforme à la revendication 1, **caractérisé en ce que** ledit composé polymère est choisi dans l'ensemble comprenant :

a) un terpolymère que l'on peut obtenir en faisant polymériser de l'éthylène avec

1) au moins un ester acrylique de formule

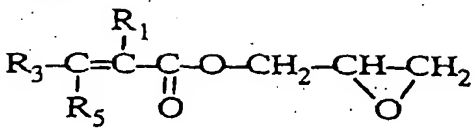


(I)

dans laquelle

R_1 représente un atome d'hydrogène ou un groupe méthyle,
R_2 représente un groupe hydrocarboné alkyle ou aryle, linéaire ou ramifié et comportant de 1 à 10 atomes de carbone, et de préférence un groupe phényle, et
R_3 représente un atome d'hydrogène ou un groupe hydrocarboné alkyle ou aryle, linéaire ou ramifié et comportant de 1 à 10 atomes de carbone, et de préférence un groupe phényle,

et 2) au moins un ester de glycidyle de formule

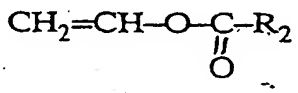


(IV)

dans laquelle
R_1 représente un atome d'hydrogène ou un groupe méthyle, et R_3 et R_5 représentent chacun, indépendamment, un atome d'hydrogène ou un groupe hydrocarboné alkyle ou aryle, linéaire ou ramifié et comportant de 1 à 10 atomes de carbone, et de préférence un groupe phényle ;

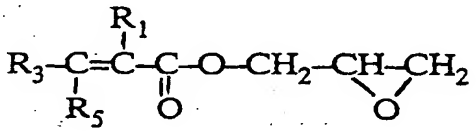
b) un terpolymère que l'on peut obtenir en faisant polymériser de l'éthylène avec

1) au moins un ester vinylique d'acide carboxylique de formule



(II)

dans laquelle
R_2 représente un groupe hydrocarboné alkyle ou aryle, linéaire ou ramifié et comportant de 1 à 10 atomes de carbone, et de préférence un groupe phényle,
et 2) au moins un ester de glycidyle de formule

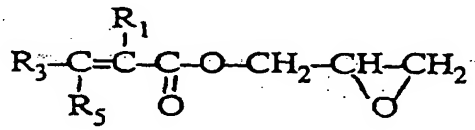


(IV)

dans laquelle

R_1 représente un atome d'hydrogène ou un groupe méthyle, et
R_3 et R_5 représentent chacun, indépendamment, un atome d'hydrogène ou un groupe hydrocarboné alkyle ou aryle, linéaire ou ramifié et comportant de 1 à 10 atomes de carbone, et de préférence un groupe phényle ;

c) un copolymère que l'on peut obtenir en faisant polymériser de l'éthylène avec au moins un ester de glycidyle de formule



(IV)

dans laquelle
R_1 représente un atome d'hydrogène ou un groupe méthyle, et R_3 et R_5 représentent chacun, indépendamment, un atome d'hydrogène ou un groupe hydrocarboné alkyle ou aryle, linéaire ou ramifié et comportant de 1 à 10 atomes de carbone, et de préférence un groupe phényle.

3. Câble électrique conforme à la revendication 1, **caractérisé en ce que** ladite base polymère en polyoléfine comporte un polymère choisi dans l'ensemble constitué par les homopolymères polyéthylènes haute densité, moyenne densité et basse densité, les copolymères et terpolymères d'éthylène et d'alpha-oléfine dont la molécule comporte de 3 à 20 atomes de carbone, les terpolymères d'éthylène, d'alpha-oléfine et de diène, et les mélanges de ces polymères.

4. Câble électrique conforme à la revendication 2, **caractérisé en ce que** ledit ester de glycidyle, au nombre d'au moins un, est du méthacrylate de glycidyle.

5. Câble électrique conforme à l'une des revendications précédentes, **caractérisé en ce que** ladite base polymère en polyoléfine contient en outre au moins un agent de réticulation, en une quantité efficace.

6. Câble électrique conforme à la revendication 5, **caractérisé en ce que** ledit agent de réticulation, au nombre d'au moins un, est du peroxyde de t-butyle et de cumyle.

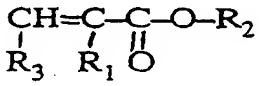
7. Câble électrique conforme à l'une des revendications précédentes, **caractérisé en ce que** ladite base polymère en polyoléfine contient en outre au moins un agent antioxydant, en une quantité efficace.

8. Composition de polymère à base de polyoléfine, résistante à la formation d'arborescences d'eau, destinée en particulier à la fabrication de gaines isolantes pour câbles électriques, et contenant une base polymère en polyoléfine, cette composition de polymère comportant, en parties en poids rapportées à son poids total, de 0,5 à 15 parties de groupes esters et de 0,01 à 5 parties de groupes époxy,
caractérisé en ce que ces quantités de groupes ester et de groupes époxy sont apportées dans la composition de polymère par un composé polymère qui comporte des groupes ester et des groupes époxy et dont l'indice de fluidité à chaud vaut de 0,1 à 40 g/10 min.

9. Composition de polymère conforme à la revendication 8,
caractérisée en ce que ledit composé polymère est choisi dans l'ensemble comprenant :

a) un terpolymère que l'on peut obtenir en faisant polymériser de l'éthylène avec

1) au moins un ester acrylique de formule

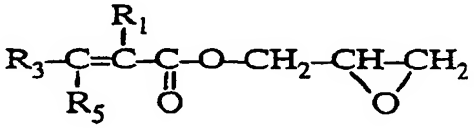


(I)

dans laquelle

R_1 représente un atome d'hydrogène ou un groupe méthyle,
R_2 représente un groupe hydrocarboné alkyle ou aryle, linéaire ou ramifié et comportant de 1 à 10 atomes de carbone, et de préférence un groupe phényle, et
R_3 représente un atome d'hydrogène ou un groupe hydrocarboné alkyle ou aryle, linéaire ou ramifié et comportant de 1 à 10 atomes de carbone, et de préférence un groupe phényle,

et 2) au moins un ester de glycidyle de formule



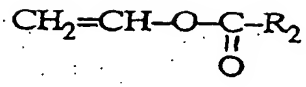
(IV)

dans laquelle

R_1 représente un atome d'hydrogène ou un groupe méthyle, et
R_3 et R_5 représentent chacun, indépendamment, un atome d'hydrogène ou un groupe hydrocarboné alkyle ou aryle, linéaire ou ramifié et comportant de 1 à 10 atomes de carbone, et de préférence un groupe phényle ;

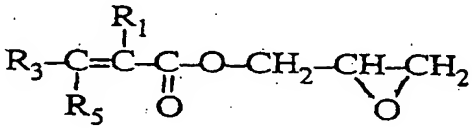
b) un terpolymère que l'on peut obtenir en faisant polymériser de l'éthylène avec

1) au moins un ester vinylique d'acide carboxylique de formule



(II)

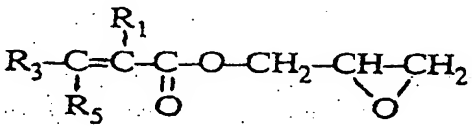
dans laquelle
R_2 représente un groupe hydrocarboné alkyle ou aryle, linéaire ou ramifié et comportant de 1 à 10 atomes de carbone, et de préférence un groupe phénylе,
et 2) au moins un ester de glycidyle de formule



(IV)

dans laquelle
R_1 représente un atome d'hydrogène ou un groupe méthyle, et R_3 et R_5 représentent chacun, indépendamment, un atome d'hydrogène ou un groupe hydrocarboné alkyle ou aryle, linéaire ou ramifié et comportant de 1 à 10 atomes de carbone, et de préférence un groupe phényle ;

c) un copolymère que l'on peut obtenir en faisant polymériser de l'éthylène avec au moins un ester de glycidyle de formule



(IV)

dans laquelle

R_1 représente un atome d'hydrogène ou un groupe méthyle, et
R_3 et R_5 représentent chacun, indépendamment, un atome d'hydrogène ou un groupe hydrocarboné alkyle ou aryle, linéaire ou ramifié et comportant de 1 à 10 atomes de carbone, et de préférence un groupe phényle.

10. Composition de polymère conforme à la revendication 8, **caractérisé en ce qu'**elle comporte un polymère choisi dans l'ensemble constitué par les homopolymères polyéthylènes haute densité, moyenne densité et basse densité, les copolymères et terpolymères d'éthylène et d'alpha-oléfine dont la molécule comporte de 3 à 20 atomes de carbone, les terpolymères d'éthylène, d'alpha-oléfine et de diène, et les mélanges de ces polymères.

11. Composition de polymère conforme à la revendication 8, **caractérisé en ce que** ledit ester de glycidyle, au nombre d'au moins un, est du méthacrylate de glycidyle.

12. Composition de polymère conforme à l'une des revendications 8 à 11, **caractérisé en ce qu'**elle contient en outre au moins un agent de réticulation, en une quantité efficace.

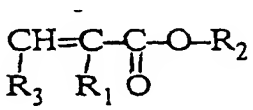
13. Composition de polymère conforme à la revendication 12, **caractérisé en ce que** ledit agent de réticulation, au nombre d'au moins un, est du peroxyde de t-butyle et de cumyle.

14. Composition de polymère conforme à l'une des revendications précédentes, **caractérisé en ce qu'**elle contient en outre au moins un agent antioxydant, en une quantité efficace.

15. Emploi d'une composition de polymère conforme à l'une des revendications 8 à 14 pour l'isolation de câbles électriques.

16. Emploi d'un terpolymère que l'on peut obtenir en faisant polymériser de l'éthylène avec

1) au moins un ester acrylique de formule

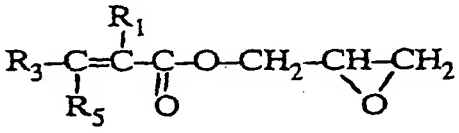


(I)

dans laquelle

R_1 représente un atome d'hydrogène ou un groupe méthyle
R_2 représente un groupe hydrocarboné alkyle ou aryle, linéaire ou ramifié et comportant de 1 à 10 atomes de carbone, et de préférence un groupe phényle, et
R_3 représente un atome d'hydrogène ou un groupe hydrocarboné alkyle ou aryle, linéaire ou ramifié et comportant de 1 à 10 atomes de carbone, et de préférence un groupe phényle,

et 2) au moins un ester de glycidyle de formule



(IV)

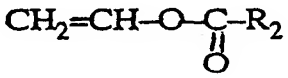
dans laquelle

R_1 représente un atome d'hydrogène ou un groupe méthyle, et
R_3 et R_5 représentent chacun, indépendamment, un atome d'hydrogène ou un groupe hydrocarboné alkyle ou aryle, linéaire ou ramifié et comportant de 1 à 10 atomes de carbone, et de préférence un groupe phényle,

en tant qu'agent retardant l'apparition d'arborescences d'eau dans une composition de polymère destinée au gainage de câbles électriques.

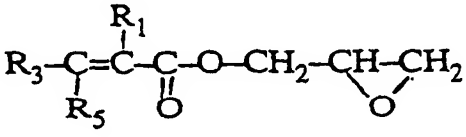
17. Emploi d'un terpolymère que l'on peut obtenir en faisant polymériser de l'éthylène avec

1) au moins un ester vinylique d'acide carboxylique de formule



(II)

dans laquelle
R_2 représente un groupe hydrocarboné alkyle ou aryle, linéaire ou ramifié et comportant de 1 à 10 atomes de carbone, et de préférence un groupe phényle,
et 2) au moins un ester de glycidyle de formule



(IV)

dans laquelle

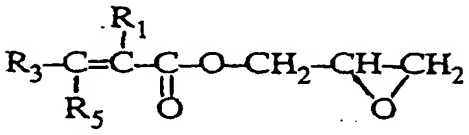
R_1 représente un atome d'hydrogène ou un groupe méthyle, et
R_3 et R_5 représentent chacun, indépendamment, un atome d'hydrogène ou un groupe hydrocarboné alkyle ou aryle, linéaire ou ramifié et comportant de 1 à 10 atomes de carbone, et de préférence un groupe phényle,

en tant qu'agent retardant l'apparition d'arborescences d'eau dans une composition de polymère destinée au gainage de câbles électriques.

18. Emploi conforme à la revendication 16 ou 17, **caractérisé en ce que** ledit terpolymère présente un indice de fluidité à chaud qui vaut de 0,1 à 40 g/10 min.

19. Emploi conforme à la revendication 16 ou 17, **caractérisé en ce que** ledit ester de glycidyle, au nombre d'au moins un, est du méthacrylate de glycidyle.

20. Emploi d'un copolymère que l'on peut obtenir en faisant polymériser de l'éthylène avec au moins un ester de glycidyle de formule :



(IV)

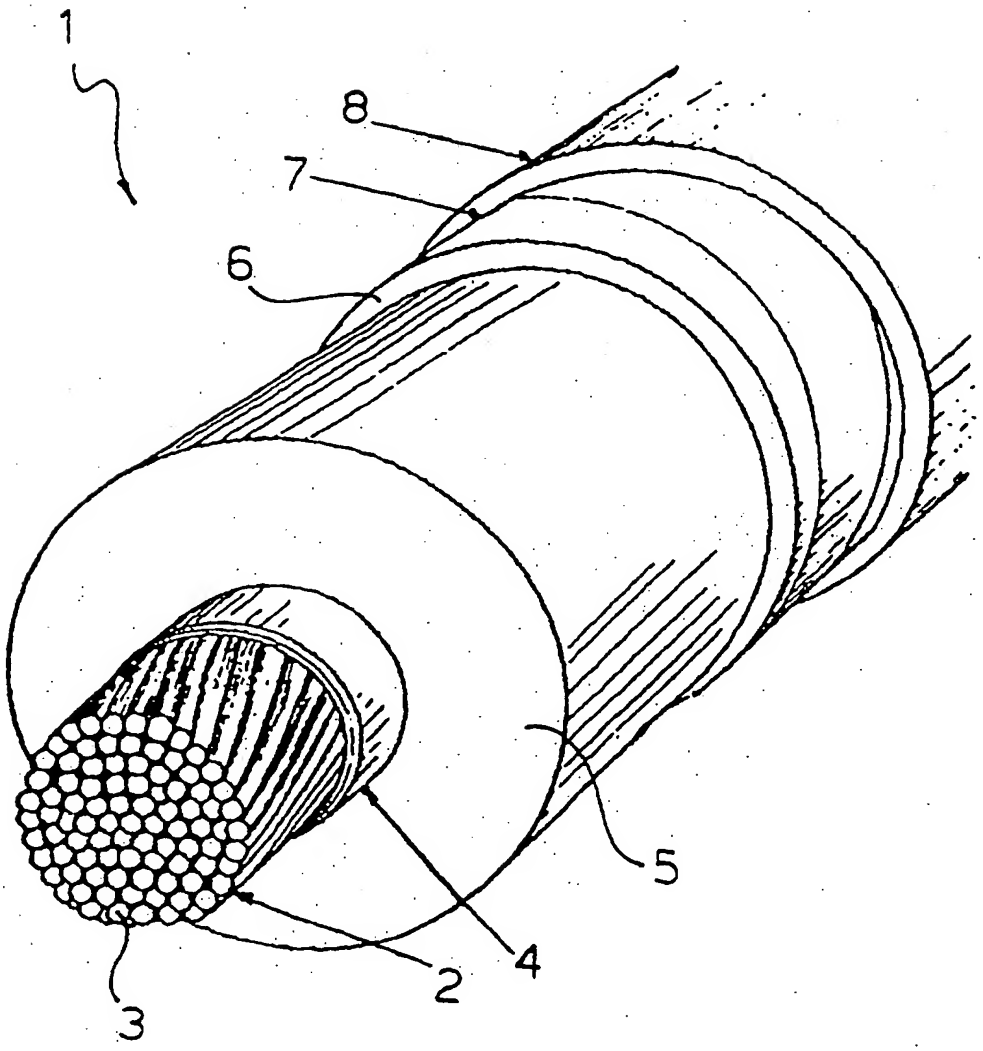
dans laquelle

R_1 représente un atome d'hydrogène ou un groupe méthyle, et
R_3 et R_5 représentent chacun, indépendamment, un atome d'hydrogène ou un groupe hydrocarboné alkyle ou aryle, linéaire ou ramifié et comportant de 1 à 10 atomes de carbone, et de préférence un groupe phényle,

en tant qu'agent retardant l'apparition d'arborescences d'eau dans une composition de polymère destinée au gainage de câbles électriques.

21. Emploi conforme à la revendication 20, **caractérisé en ce que** ledit ester de glycidyle, au nombre d'au moins un, est du méthacrylate de glycidyle.

22. Emploi conforme à la revendication 20, **caractérisé en ce que** ledit copolymère présente un indice de fluidité à chaud qui vaut de 0,1 à 40 g/10 min.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